



(11) (A) No. 1 195 791

(45) ISSUED 851022

(52) CLASS 400-5150  
C.R. CL. 18-640;  
204-91.33; 400-1000;  
400-4022; 400-7002

(51) INT. CL. C09D 11/02, B41M 1/24

(19) (CA) **CANADIAN PATENT** (12)

(54) Radiation Curable Growth Controlling Printing Ink  
Compositions for Chemically Embossing Heat-Foamable  
Material

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(21) APPLICATION No. 423,882

(22) FILED 830317

(30) PRIORITY DATE U.S.A. (417,008) 820913

No. OF CLAIMS 12 - NO DRAWING

**Canada**

BACKGROUND OF THE INVENTION1. Field of the Present Invention:

The present invention relates to foam-controlling printing ink compositions of use for chemically embossing of floor, ceiling or wall coverings, and like articles.

## 2. Description of the Prior Art:

Chemical embossing techniques have been used widely in the manufacture of floor, ceiling and wall coverings, as described in U.S. Pat. 3,293,094 and 3,293,108, to Nairn, et al. Such chemical embossing techniques normally have involved coating a base material with a substantially uniform layer of a resinous material. The resinous material includes a foaming or blowing agent uniformly dispersed therein, and which is adapted, upon subsequent heating, to decompose and to liberate gaseous decomposition products to expand and create a foamed, blown resinous product.

One aspect of such chemical embossing techniques has comprised the printing of selected, predetermined areas of the surface of the heat-foamable resinous material, prior to the heating, with a solvent foam-growth-controlling printing ink composition which is capable of affecting and changing the degree of foam-growth of those selected, predetermined areas, when the heat-foamable resinous materials are subsequently heated to the required elevated temperature.

Such solvent foam-growth-controlling printing ink compositions have contained either: (1) agents for inhibiting or suppressing the decomposition of the foaming or blowing agents to thus decrease the resulting expanding gaseous action on the foamable resinous materials and to correspondingly decrease the foam-growth in the selected, predetermined areas to which they are applied; or (2) agents for catalyzing or accelerating the decomposition of the foaming or blowing agents to thus increase

the resulting gaseous action on the foamable resinous materials and to correspondingly increase the foam-growth in the selected, predetermined areas to which they are applied.

As a consequence, the surface of the resulting, foamed or blown resinous materials have been given an embossed or relief pattern effect containing relatively higher areas or lands and relatively lower areas or valleys, thus providing excellent surface interest.

The solvent foam-growth-controlling printing ink compositions have thus contained both: (1) the foam-growth-controlling agents; and (2) the pigments, ink, dyes or other coloring materials, whereby the resulting embossed or relief pattern effects have been made to coincide very accurately and very precisely with the ink-printing pattern, thus creating excellent visual and tactile effects which are in substantially perfect alignment and registry at all times.

A number of organic solvent-based foam-growth-controlling printing ink compositions as described in said patents, have been used previously in such chemical embossing manufacturing techniques, and have proved to be relatively successful therein. However, organic <sup>solvent</sup> ~~solvent~~-based printing inks are relatively expensive, are usually very difficult to remove or clean from printing equipment, are occasionally not adaptable for use with conventional commercial printing equipment, are often flammable or have relatively low flash points which are unfortunately conducive to dangerous or hazardous conditions, frequently cause significant waste, ecological, or pollution problems, and sometimes require costly and time-consuming solvent-recovery programs.

An improved solvent, growth-controlling printing ink composition is described in U.S.Pat. 4,083,907. These compositions employ aqueous-alcohol as solvents and are advantageous as compared to organic solvent inks in that they do not pollute the atmosphere excessively. However, they require a large amount of heat energy to remove the aqueous-alcoholic solvents.

Accordingly, it would be of considerable advantage to the industry to provide a solventless, foam-growth controlling printing ink composition for use with chemical embossing processes, which compositions are particularly adapted to require less heat energy than in the past which do not create dangerous or hazardous conditions, or create significant waste, ecological or pollution problems; and which enable the production of commercial embossed flooring products using economical manufacturing equipment and processes.

#### SUMMARY OF THE INVENTION

The present invention provides a solventless, radiation curable growth-controlling printing ink composition for chemically embossing heat foamable material, which composition includes about 5% to about 99% of a radiation curable vehicle, about 1% to about 25% of a foam-controlling chemical agent about 0.1% to about 95% of a pigment, and about 0.1% to about 15% of a photo-initiator. Such an ink composition is capable of being readily printed onto the foamable material and cured using radiation energy to provide a film surface which is non-tacky, non-crocking and non-blocking, and which exhibits good adhesion to both the foamable material

and to the wear layer.. After blowing, effectively embossed flooring product is formed.

DETAILED DESCRIPTION OF THE  
PREFERRED EMBODIMENTS OF THE INVENTION

The Foam-Growth Controlling Agent:

The radiation curable foam-growth-controlling printing ink compositions for controlling the foam-growth of heat-foamable and expandable resinous materials upon heating includes a foam-growth controlling agent, which is present in an amount of at least about 1% and normally up to about 25% by weight, based upon the total weight of the printing ink composition. The amount of the foam-growth controlling agent used will depend upon the degree of the embossing effect which is desired or required.

Another complete list of suitable foam-growth controlling agents is described in the aforementioned Nairn patents. The preferred commercial foam-controlling agents are trimellitic anhydride and benzotriazole, although many others known in the art may be used as well. Such foam-growth controlling agents must be sufficiently soluble or dispersible in the printing ink compositions and they must be sufficiently stable therein as not to be convertible, through reaction with the radiation curable vehicle, or otherwise, into other chemical forms in which they lose their foam-growth controlling properties and characteristics.

The Radiation Curable Vehicle:

The radiation curable vehicle of the printing ink composition of the invention functions to hold the pigment component of the ink in dispersion and, when cured, as a binder in the resulting film coating. Accordingly, any radiation curable resin system which has a suitable viscosity to disperse the pigment and which forms a flexible coating upon curing which is adherent to both the foam and wear layers may be used. Such reactive resin systems are well known in the art, and are described in such U.S. patents as 4,100,318; 4,180,615; 3,924,023; 4,122,225; 4,309,452; 3,485,732; and 4,196,243.

Generally the components of a preferred radiation curable vehicle in the printing ink composition of the present invention includes one or more of an unsaturated resin, a reactive monomer, and a multifunctional monomer, and, if desired, an <sup>INERT</sup> ~~inert~~ polymer resin. The unsaturated resins are usually low molecular weight polymers or oligomers containing a functional group which participates in the polymerization process. The unsaturated resins commonly employed herein are compounds which contain polar groups, preferably urethanes. However, polyethers, epoxides, amides and the like terminated by two or more photopolymerizable ethylenically unsaturated groups can be employed.

The reactive monomers preferably includes those containing at least one acrylyl or methacryl group, or are lighter alkyl acrylamides and methacrylamides. Illustrative of which one can mention acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, butoxyethyl

acrylate, dicyclopentenyl acrylate, isodecyl acrylate, 2-phenox-yethyl acrylate, glycidyl acrylate, 2-ethoxyethyl acrylate, 2-methoxyethyl acrylate, 2-(N, N-diethylamino) ethyl acrylate, trimethoxyallyloxymethyl acrylate, vinyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl acrylate, (methylcarbamy) etlyl acrylate and the corresponding methacrylates; and nonyl and dodecyl acrylamides and methacrylamides. However, other photo curable, monofunctional monomers known in the art may be used as well. Other reactive monomers, such as vinyl pyrrolidone, also may be included with the reactive monomer to aid in dispersing the pigment and to improve the flexibility of the resultant film coating.

Multifunctional monomers may be added along with the reactive monomers when it is desired to increase the cross-link density of the coating while preserving the flexibility of the film. The multifunctional monomers are preferably of the acrylyl type, such as neopentyl glycol diacrylate, pentacrytanitol triacrylate, 1, 6-hexane dioldiacrylate, trimethylolpropane triacrylate and the like. The multifunctional monomers listed above are for illustrative purposes only. As with the reactive monomers given above, any multifunctional monomers capable of curing on exposure to radiation are suitable.

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The <sup>INERT</sup> ~~inert~~ resin is a polymeric material which does not contain any unsaturation; it helps in film formation, adherence and to increase the viscosity of the vehicle. Generally the <sup>INERT</sup> ~~inert~~ resins are polyolefins and modified polyolefins, the vinyl polymers, the polyethers, the polyesters, the polylactones, the polyamides, the polyurethanes, the polyureas, the polysiloxanes, the polysulfies, the polysulfones, the polyformaldehydes, the phenol-formaldehyde polymers, the natural and modified natural polymers, the heterocyclic polymers, and the like.



Illustrative of these polymers are the acrylic polymers such as poly (acrylic acid), poly (methyl acrylate), poly-(ethyl acrylate), poly (methacrylic acid), poly (methyl methacrylate), poly (ethyl methacrylate); poly (vinyl chloride); poly (vinyl alcohol); poly (ethylene/propylene/5-ethylidenebicyclo (2.2.1)-hept-2-ene); polyethylene; polypropylene; synthetic rubbers, e.g.; butadiene/acrylonitrile copolymers and chloro-2-butadiene 1,3 polymers; the polyesters, copolyesters, polyamides and copolyamides, such as polycaprolactone, poly (caprolactone/vinyl chloride) poly (ethylene glycol terephthalate), poly (hexamethylene succinate), poly (hexamethylene maleate), poly (hexamethylene carbonate), poly (caprolactam), poly (hexamethylene adipamide), and the like; the polyethers such as poly (glutaraldehyde), polyethylene oxide, polypropylene oxide, poly (tetrahydrofuran), polycyclohexene oxide, copolymers of ethylene oxide and propylene oxide with starters containing reactive hydrogen atoms such as the mixed copolymers using ethylene glycol, glycerol, sucrose, etc., as the starter; vinylidene polymers and copolymers, e.g., vinylidene chloride/acrylonitrile, vinylidene chloride/methacrylate and vinylidene chloride/vinyl acetate polymers; ethylene/vinyl acetate copolymers; the polyureas and polyurethanes, such as described in Polym<sup>U</sup>urethanes: Chemistry and Technology, Volumes I and II, <sup>SAUNDERS</sup>~~Saunders~~ and Frisch, published by Interscience Publishers; the polycarbonates; polystyrenes; polyvinyl acetals, e.g., polyvinyl butyral, polyvinyl formal; the cellulose ethers, e.g., methyl cellulose, ethyl cellulose, and benzyl cellulose; the cellulose

esters, e.g., cellulose acetate, cellulose acetate succinate and cellulose acetate butyrate; as well as the natural and modified natural polymers such as gutta percha, cellulose, gelatin, starch, silk, wool, and the like; the siloxane polymers and copolymers; the formaldehyde polymers such as polyformaldehyde; formaldehyde resins such as phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde, aniline-formaldehyde and acetone-formaldehyde; phenolic resins and the like.

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In general, the amount of radiation curable vehicle used in the ink composition of the invention will depend <sup>upon</sup> ~~upon~~ the amount of pigment needed for the degree of color desired, its particle size, and the viscosity of the vehicle. Usually the ink composition includes about 5% to 99% of the radiation curable vehicle and preferably about 10-90%. The unsaturated resin may comprise 0-99% of the vehicle, the reactive and multifunctional monomers 0-99%, and the <sup>INERT</sup> ~~inert~~ resin 0-30% by weight of the vehicle.

To assure a flexible film having good adhesion to the foam before curing, and to the wear layer after curing, it is preferable that the ink composition contain from 0.1 to less than 1 equivalent of curable vehicle, material per 500g. of the ink composition.

#### PHOTOINITIATORS

The curing reaction can be initiated by either UV radiation or high energy ionizing radiation. The UV radiation can be obtained from sunlight or special light sources which emit significant amounts of UV light having a wavelength in the range of

about 2000 to about 4000 Angstrom units. When UV radiation is used for the curing reaction, a dose of 0.0004 to 60 watts/centimeter is employed.

When U.V. radiation is used for curing, a photoinitiator is added to the composition to increase the photopolymerization or photocuring reaction rate. Various photoinitiators and co-initiators are operable and well known to those skilled in the art. Examples of photoinitiators include, but are not limited to, valerophenone, acetophenone, dibenzosuberone, 4-aminobenzophenone, hexanophenone,  $\alpha$ -tetralone, 9-fluorenone, thioxanthene-9-one, 7-H-benz(de)anthracene-7-one, 4,4'-bis(dimethylamino)benzophenone, o-methoxybenzophenone, triphenylphosphine, tri-o-tolylphosphine, benz(a)anthracene-7, 12-dione, benzoin isopropyl ether, benzoin isobutyl ether, benzoin tetrahydropyranyl ether, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, thioxanthrone, 3-methoxybenzophenone, 4-methoxybenzophenone, benzophenone, 4,4'-dimethoxybenzophenone, 4-methoxybenzaldehyde, 4-methoxyacetophenone, benzaldehyde, dibenzosuberone, ethyl benzoin ether, isobutyl benzoin ether,  $\alpha,\alpha$ -diethoxy- $\alpha$ -phenylacetophenone,  $\alpha$ -methylolbenzoinmethyl ether,  $\alpha,\alpha$ ,  $\alpha$ -trichloroacetophenone and 2,3-butanedione and mixtures thereof, which service to give greatly reduced exposure times and thereby, when used in conjunction with various forms of energetic radiation, yield very rapid, commercially practical time cycles by the practice of the instant invention.

THE PIGMENT

By the term "pigment" as used herein is meant those colored organic and inorganic compounds which are normally used in the art to impart color as well as organic dyes which are used for the same purpose. There is no restriction as to pigments or dyes except that they be nonreactive to the components of the ink. Illustrative of the various inorganic pigments are titanium dioxide, carbon black, metallic flakes, powders and dusts such as aluminum powder, bronze powder, and the like. Organic pigments and dyes which can be used include Phthalocyanine green, Phthalocyanine blue, Permanent red 2B, Lithol red, Lithol rubine, Toluidine red, Hansa yellow, Toluidine yellow, oil soluble dyes, and the like.

There is no particular criticality in respect to the amount of coloring material to be used. However, sufficient colorant should be used to provide good covering properties with the proper density of color. While economic factors generally determine the maximum amount of pigment to be used, it goes without saying that pigments should not be used in such amounts as to cause the ink to chalk on drying, or to make the viscosity of the ink unreasonably high. Naturally the specific amount of pigment used is dependent upon the coloring properties of the pigment, the properties of the inks and so forth.

Most any commercial pigment can be used with this ink system. Among them are rhodamines, rubines, lithols, red lake C, 2-B reds, phthalo blues and greens, carbon blacks, alkali blues, methyl violets, moly oranges, benzidine yellows, chrome yellows

carbazole violets, etc. Pigments that do not inhibit the polymerization of the reactive monomers are preferred.

In addition to the essential components of the curable composition of the invention set forth above, additional materials may be added in order to obtain the necessary properties for a legend ink. These are listed in the Table below in their respective proportions by weight.

TABLE

Component	Broadly % by Wt.	Preferably % by Wt.
Inhibitors	.01-1	.05-0.2
Fillers	30-70	45-55
Thixotropic Agent	0-4.0	0-2.0
Levelling Agent	0.05-2.0	0.1-1
Coinitiators	0.05-1.5	0.05-0.2

The choice of the materials and the amounts used may be readily determined by those skilled in the art.

PROPERTIES OF FILM OF GROWTH-CONTROLLING  
RADIATION CURABLE PRINTING INK COMPOSITION  
ON FOAMABLE RESINOUS LAYER

In general, to form a non-tacky, non-crocking and non-blocking film coating, it is preferable that at least 50% of the radiation curable vehicle be cured, and within a reasonable time. Any liquid remaining after radiation curing will be absorbed into the pigment and will cure thermally during subsequent operations.

The inks of the invention can be printed by any conventional method, including rotogravure and screen printing. Usually for rotogravure printing a lower viscosity ink is used

while for screen printing a higher viscosity or even a paste ink may be used.

In commercial applications, these inks can be cured at speeds ranging from 260 to 500 fpm. The speed of cure depends largely on the number of lamps being used and the color of the ink being photopolymerized. For instance, an ultra violet curable yellow colored metal decorating ink of this invention can be cured at speeds up to 400 fpm using two 200 watt per linear inch lamps while a black ink of the same invention would require five 200 watt per linear inch lamps to cure at the same speed. Preferably the inks are cured in an air atmosphere in which the adhesion of the ink film to the wear layer is improved.

The invention will be illustrated with reference to the following examples:

#### EXAMPLES

##### Example 1

<u>Component of Ink Composition</u>	<u>Parts by Wt.</u>
<u>Radiation Curable Vehicle</u>	
Dicyclopentenyl oxyethyl methacrylate	31.17
Vinyl pyrrolidone	44.01
Vinyl chloride-Vinyl acetate copolymer	6.41
<u>Foam-Growth Controlling Agent</u>	
Trimellitic anhydride	9.09
<u>Photoinitiator</u>	
Benzophenone	2.68
Sandoray <sup>*</sup> 1000	2.68
<u>Pigment</u>	
Microolith 1095-K60	3.96

The components are mixed, 40 drops of FC170C surfactant are added, and the ink composition is printed on selected, pre-

determined areas of a gelled, foamable plastisol formulated by mixing the following ingredients on a Cowles mixer:

	Parts
Polyvinyl chloride, dispersion grade, specific viscosity 0.6	50
Polyvinyl chloride, dispersion grade, specific viscosity 0.4	50
Butyl benzyl phthalate plasticizer	25
Di-(2-ethyl hexyl) phthalate plasticizer	45
Titanium dioxide pigment (55% solids)	7
Azodicarbonamide blowing agent	3
V. M. & P. naphtha (boiling range 190°-275°F.)	5

Heating at 375°F. decomposes the azodicarbonamide blowing agent to create the desired blowing and foaming function. An embossing depth of about 26 mils is obtained at about 59 mils foam. a wear layer of about 10 mils is used. The foam-growth controlling properties and characteristics of the printing ink composition are well demonstrated in this Example.

The film then is cured under two UV lamps 200/200 watts in a nitrogen atmosphere containing 80 ppm oxygen, the infrared temperature being 160°F.

#### ADDITIONAL EXAMPLES

##### Example 2

Dicyclopentenyl oxymethacrylate	45.53
Diacrylate of bis-phenol diglycidylether	9.54
Vinyl pyrrolidone	34.76
Trimellitic anhydride (8g)	17.68
Benzophenone	2.86
Sandoray*1000	2.86
Pigment BR-K	4.22
Tergetol*4	1.94

The curing was carried out in an air atmosphere and the adhesion was excellent.

\* TRADE MARK

Example 3

Acrylated urethane	10.00
Vinyl pyrrolidone	90.00
Trimellitic anhydride	10.00
Benzophenone	0.50
Sandoray*1000	0.05
Pigment	10.00

Example 4

Dicyclopentenylloxyethyl methacrylate	27.44
Vinyl pyrrolidone	38.74
Vinyl chloride-vinyl acetate copolymer	6.41
Tolyltriazole	19.97
Photoinitiator	4.72
Pigment	3.48

Although several specific Examples of the inventive concept have been described, the same should not be construed as limiting the broader aspects of the present invention which include other equivalent features and materials, as set forth and defined in the appended claims.



What is Claimed Is:

1. A radiation curable growth-controlling printing ink composition for chemically embossing heat-foamable material which composition is capable of being applied selectively to said foamable material and cured by radiation to provide a film which is non-tacky, non-crocking and non-blocking comprising:

a radiation curable vehicle;  
a foam-controlling chemical agent therein which is non-reactive with said vehicle and diffusable into said foamable material upon curing said vehicle;  
a pigment, and  
a photoinitiator.

A 2. A radiation curable growth-controlling printing ink composition according to Claim 1 in which said radiation curable vehicle has unsaturated compounds with at least 0.1 to less than 1 equivalents of unsaturated bonds per <sup>500 g</sup>~~500g~~ of said ink composition.

3. A solventless radiation curable growth controlling printing ink composition according to Claim 1 comprising about 5% to about 99% of said radiation curable vehicle, about 1% to about 25% of said foam-controlling chemical agent, about 0.1% to about 95% of said pigment, and about 0.1% to about 15% of said photoinitiator, by weight of said composition.

4. A radiation curable printing ink composition according to Claim 1 in which said radiation curable vehicle includes one or

more components selected from an unsaturated resin, a reactive monomer, and a multifunctional monomer and, optionally, an inert polymeric resin.

5. A radiation curable printing ink composition according to Claim 1 includes 10-90% of said radiation curable vehicle.

6. A radiation curable printing ink composition according to Claim 1 in which such foam-controlling chemical agent acts as an inhibitor for any blowing agent present in the heat foamable material.

7. A flooring article of manufacture comprising:

- a foamable gel, and
- a radiation curable ink of Claim 1 coated on said gel.

8. A flooring product comprising:

- a foamable gel,
- a radiation cured growth-controlling printing ink of the composition of Claim 1 coated on said gel, and
- a wear layer on said gel,

said coating exhibiting good adhesion with the gel and the wear layer.

9. A method of making a chemically embossed flooring product comprising:

- providing a heat foamable material,
- applying a radiation curable growth-controlling printing ink composition as defined in Claim 1, selectively on said material,
- curing said composition by radiation to form a film thereon, and
- foaming said material in the presence of said growth controlling chemical agent.

10. A method according to Claim 9 including the additional step of applying a wear layer on said foamable material.

11. A method according to Claim 9 in which at least 50% of the radiation curable material in said composition is cured.

12. A method according to Claim 9 in which said film exhibits good adhesion between both foam material and said wear layer.